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## (56) Documents Cited

GB 2261226 A	EP 0725161 A1	EP 0387904 A1
WO 96/24703 A1	WO 89/05361 A1	US 5487922 A
US 5436035 A	US 4941430 A	US 4269137 A

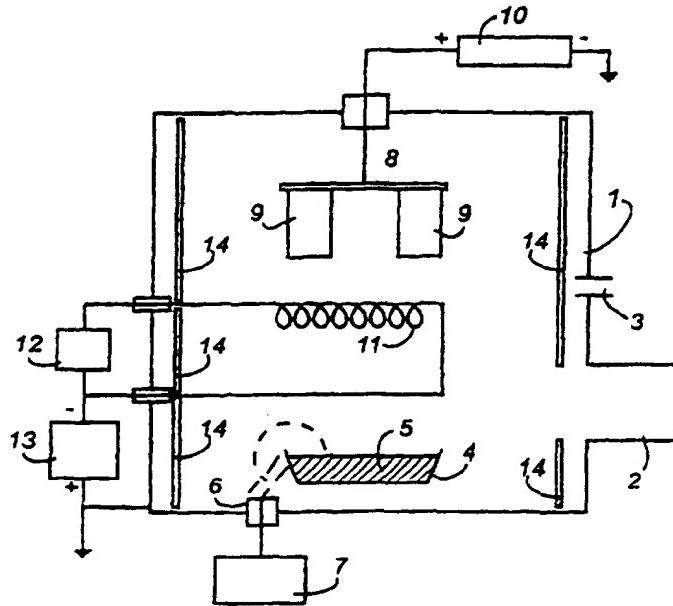
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## (54) Abstract Title

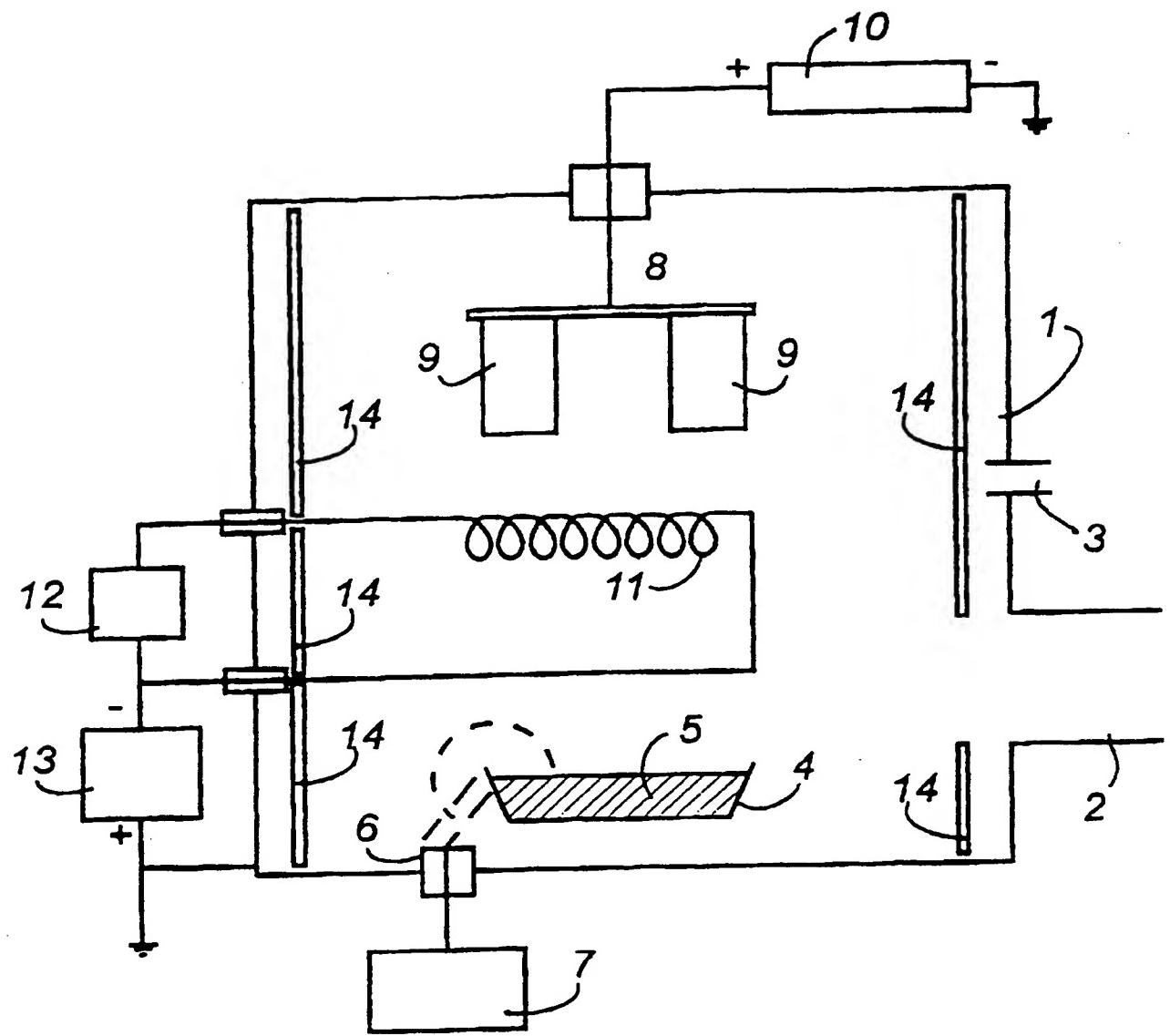
Depositing a coating on a conductive substrate using positive bias and electron bombardment

(57) Depositing a coating on a conductive substrate includes applying a positive d.c. bias to the conductive substrate and subjecting the substrate to electron bombardment before and/or during deposition of the coating. The coating may be applied by physical vapour deposition and is preferably zirconia. In one embodiment the positive d.c. bias and a negative d.c. bias are applied alternately to the substrate. Sputter cleaning can also be carried out prior to deposition.



GB 2 323 855 A

1/1



**METHOD AND APPARATUS FOR DEPOSITING  
A COATING ON A CONDUCTIVE SUBSTRATE**

This invention relates to methods and apparatus for depositing a coating on a conductive substrate. The invention has considerable, though not exclusive, relevance to the deposition of metallic oxides onto conductive substrates, in particular, the metallic oxide zirconia. Whilst normally electrically insulating, zirconia becomes conducting at higher temperatures. The exact temperature will depend on the purity and structure of the coating material, but typically temperatures greater than 700°C are needed to achieve appreciable electrical conductivity.

Zirconia is an interesting material for many technological applications, especially because of its low thermal conductivity and thus its excellent thermal insulation properties. These properties are useful, for example, in the regions of gas turbine engines where combustion takes place, to protect components such as turbine blades from thermal degradation.

In order to ensure coating purity and effectively control the deposition species, a number of vacuum-based coating processes

are in current use. These fall into two groups. The first employs substrate heating, by means such as radiant heaters in the coating chamber, to raise the substrate temperature; this ensures that the resulting coating, after being deposited onto the heated substrate, has improved adhesion and has a denser structure than a coating formed at near-ambient temperatures. Also, since the deposition temperature is nearer to the operating temperature of the turbine, any in-service thermally induced stresses in the coating, caused by differential expansion or contraction of the coating relative to the substrate, will be reduced. Usually, electron beam evaporation is used to produce the coating.

There are several disadvantages of this system. One is that the adhesion of the coating (whilst improved) may still not be adequate; a second is that the heating arrangement can limit the space available within the deposition chamber, and can be inefficient in terms of electrical power consumption.

The second group of vacuum-based coating processes, in which there has been much recent research interest, employs plasma-assistance in the deposition process. This involves ionising a proportion of the depositing species, such that they are

accelerated to the substrate being coated which is biased negatively, either by a direct current or radio frequency supply. This can improve the adhesion and the structure of the coatings. However, for optimal effect, additional heating means are still needed.

According to one aspect of the invention there is provided a method of depositing a coating on a conductive substrate including applying a positive d.c. bias to the conductive substrate and subjecting the substrate to energetic electron bombardment before and/or during deposition of the coating.

According to another aspect of the invention there is provided an apparatus for depositing a coating on a conductive substrate comprising means for applying a positive d.c. bias to the conductive substrate and means for subjecting the substrate to energetic electron bombardment before and/or during deposition of the coating on the conductive substrate.

A distinguishing feature of the apparatus and method of the invention is the requirement for the substrate to be held at a positive d.c. bias before and/or during deposition. Direct heating of the substrate is then accomplished with great

efficiency by energetic electron bombardment which also ensures that the condition at the substrate surface is suitable for the growth of well adhered films with an excellent micro-structural morphology.

This arrangement may be combined with a plasma-assisted method such as that described in GB2261226B to produce a sequential process. However, the electron bombardment method and apparatus defined in accordance with this invention is preferably used alone, in a single stage process. Indeed, one of the advantages of the electrical bombardment method and apparatus is its relative simplicity, and low cost, by virtue of the reduction in the number of power supplies used, compared to currently available plasma processes.

A method and apparatus according to the invention are now described, by way of example only, with reference to the sole figure which is a schematic diagram of the apparatus.

Referring to the figure, the apparatus comprises a vacuum chamber 1 having a pumping port 2 which in use of the apparatus is connected to a vacuum pumping system (not shown), and a gas inlet 3. Within the chamber 1 there is provided a

crucible 4 containing the source material 5 for evaporation, for example zirconia, adjacent to an electron beam arrangement 6, such as an electron beam gun, connected to a power supply 7. Also arranged within the chamber 1 is a support 8 which carries the conductive substrates 9, i.e. components, to be coated. The support 8 is connected to a d.c. power supply 10 arranged to maintain the support 8 at a positive d.c. potential.

Between the crucible 4 and the support 8 there is provided a thermionic emitter comprising a filament 11 provided with a filament heater power supply 12 and a bias supply 13 which applies a negative d.c. bias to the filament. The filament 11 may be of any of the usual forms which will be evident to a person skilled in the art of the deposition of materials, for example a tungsten or tantalum filament.

In use, the vacuum chamber 1 is first pumped down via pumping port 2 to a pressure of less than  $10^{-5}$ Torr. The next stage may involve increasing the chamber pressure to around 10mTorr by admitting argon gas to the chamber 1 via gas inlet 3, and then negatively biasing the substrates to several hundred volts, whereby a glow discharge or plasma will be initiated which

then sputter-cleans the substrates by bombarding them with ions. This bombardment (so called "sputter-cleaning") can be intensified by heating the filament 11 and (preferably) at the same time biasing it negatively. This sputter-cleaning stage normally lasts for about twenty minutes, but is not a necessary prerequisite for the process, provided that satisfactory chemical precleaning of the substrates 9 is carried out prior to placing them in the vacuum chamber 1.

If the sputter-cleaning stage is not utilised, then the deposition process can proceed without raising the chamber pressure. Thus with a chamber pressure of about  $10^{-5}$  Torr the substrates 9 are biased positively by supply 10 to between 50 and 500 volts. At the same time, the filament 11 is heated, by passing a current through it. Electrons thus emitted are accelerated to the substrates 9 which are directly heated by the resultant energetic electron bombardment to a temperature typically greater than 700°C. The electron beam gun 6 is then activated to commence evaporation of zirconia, which ideally has an additional phase, such as yttria (typically 8 to 20 percent by weight) which stabilises the higher temperature tetragonal or cubic phases, and therefore reduces the possibility of changes in the phase composition of the coating

during in-service temperature cycling.

The coating progresses in this mode for a sufficient duration to build-up an adequate coating thickness, typically 300-400 micrometers. The thickness is determined by the required in-service temperature 'drop' across the coating, i.e. the thicker the coating the greater the thermal insulation provided and thus the lower the maximum temperature attained by the component during use.

It will be appreciated that the heated filament 11 need not be negatively biassed. Alternatively, the filament could be maintained at earth potential and, in this case, the bias supply 13 could be omitted.

However, a negatively biassed filament can be advantageous in that it enables other surfaces in the earthed chamber 1 to be heated by electron bombardment. In a specific implementation of this, shields 14 are provided inside the chamber and are thermally insulated from the chamber wall. The shields 14 can be held at earth potential (like the chamber wall), and are thereby heated by bombardment with energetic electrons which are accelerated away from the negatively biassed heated

filament 11. If the filament is at earth potential then this effect can be achieved by biasing the shields 14 positively. The shields, thus provided, are effective to maintain the substrates 9 at a relatively high temperature by reducing radiative heat loss to the exterior.

It has been found that energetic electron bombardment will take place much more effectively if the atmosphere between the heated filament 11 and the substrates 9 is electrically conducting. To this end, a small amount of an ionisable gas, e.g. argon, is preferably introduced into the chamber, via inlet 3, such that the chamber pressure is slightly higher, e.g.  $3 \times 10^{-5}$  Torr, to encourage the creation of a thermionically supported discharge between the filament 11 and the substrates 9. This discharge provides an electrically conducting path between the filament 9 and the substrates 11 and so enhances electron transport. Once deposition has commenced the ionisable species can also be derived from the coating material itself.

The foregoing processes can be further modified by using a pulsed power supply which alternates a positive then negative, then positive (etc.) bias. This allows heating by energetic

electron bombardment whilst the sample is positive and ion bombardment of the growing films during the negative bias periods provided the chamber pressure is sufficiently high to create a plasma. This offers additional control over the coating microstructure. However, for elements which can form negative ions (such as oxygen) the ion bombardment effect can occur when a positive bias is applied to the substrates. In this respect it can be beneficial to raise the chamber pressure to several mTorr to initiate a plasma during the process. This, however, can create certain disadvantages caused by ion bombardment of the filament (made typically of tungsten), as this may lead to incorporation of tungsten in the growing film. The effects of this can be mitigated by shielding the filament from the substrates, so that the whole of the filament is not in direct line-of-sight of the substrates. However, if a plasma is initiated with the substrates in the positively biased mode, the chamber walls will be cathodic in the resulting plasma or glow discharge, and there is then the danger of coating contamination by material from the walls. This can be mitigated by depositing the coating material onto the walls prior to the process. However, for a material which is electrically insulating at lower temperatures this can create plasma instabilities.

especially if no conducting cathode surface is available. Thus, although the above-described sequential process may be advantageous in some applications, it is generally preferable to deposit the entire coating at low pressure (approx. $10^{-5}$ Torr) on a positively biased component or components which is subjected to energetic electron bombardment before and/or during deposition of the coating.

Since this preferred embodiment is essentially a line-of-sight process, component rotation and traversal relative to the vapour source is usually needed to ensure adequate thickness uniformity over the component surface.

CLAIMS

1. A method of depositing a coating on a conductive substrate including applying a positive d.c. bias to the conductive substrate and subjecting the substrate to energetic electron bombardment before and/or during deposition of the coating.
2. A method as claimed in claim 1, wherein said electron bombardment is such as to heat the conductive substrate to a temperature greater than 700°C.
3. A method as claimed in claim 1 or claim 2, including applying said positive d.c. voltage in the range 50 volts to 500 volts.
4. A method as claimed in any one of claims 1 to 3, wherein said deposition takes place at a chamber pressure no greater than  $3 \times 10^{-5}$  Torr.
5. A method as claimed in any one of claims 1 to 4, including evaporating a source of the coating material so that the resultant vapour is deposited on the substrate to form the coating.

6. A method as claimed in any one of claims 1 to 5, for depositing a coating of a metal oxide.

7. A method as claimed in claim 6, for depositing a coating of zirconia.

8. A method as claimed in any one of claims 1 to 7, including sputter-cleaning the conductive substrate before the coating is deposited.

9. A method as claimed in any one of claims 1 to 8, including depositing part of the coating by a plasma-assisted physical vapour deposition technique.

10. A method as claimed in claim 9, including alternatively applying said positive d.c. bias and a negative d.c. bias to the conductive substrate whereby deposition by application of said plasma-assisted physical vapour deposition technique takes place while said negative d.c. bias is being applied.

11. An apparatus for depositing a coating on a conductive substrate comprising means for applying a positive d.c. bias to the conductive substrate and means for subjecting the

substrate to energetic electron bombardment before and/or during deposition of the coating on the conductive substrate.

12. An apparatus as claimed in claim 11, including means for evaporating a source of the coating material such that the resultant vapour is deposited on the conductive substrate to form the coating.

13. An apparatus as claimed in claim 11 or claim 12, wherein the electron bombardment means is effective to heat the conductive substrate to a temperature greater than 700°C.

14. An apparatus as claimed in claim 13, wherein the electron bombardment means is a heated filament.

15. An apparatus as claimed in claim 14, wherein said heated filament is negatively biassed relative to the deposition chamber wall.

16. An apparatus as claimed in claim 15, wherein the negatively biassed heated filament causes heating of internal shield means by energetic electronic bombardment to reduce radiative cooling of the substrate.

17. An apparatus as claimed in claim 16 wherein the internal shielding means is either held at earth potential or is positively biassed.

18. An apparatus as claimed in claim 12, wherein the evaporation means is an electron beam gun.

19. A method substantially as herein described, with reference to the accompanying drawing.

20. An apparatus substantially as herein described with reference to the accompanying drawing.



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15.

Application No: GB 9706538.7  
Claims searched: 1-20

Examiner: Peter Beddoe  
Date of search: 23 April 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C7F (FAHE, FAHX, FAXE, FAXX, FCAV, FCAX, FCD, FCF, FCVE, FCVL, FCVM, FCVX, FCXE, FCXL, FCXM, FCXX)

Int Cl (Ed.6): C23C (14/02, 14/22, 14/24, 14/32)

Other: Online: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage		Relevant to claims
Y	GB 2261226 A	(MATTHEWS) see esp claim 1	1,11 at least
X	EP 0725161 A1	(METAPLAS) see esp claim1 & col2 line 54 - col3 line 32	1,11 at least
Y	EP 0387904 A2	(MATSUSHITA) see esp claim 1, exs & figs	1,11 at least
Y	WO 96/24703 A1	(JET) see esp p10 lines 6-25 & fig 3	1,11 at least
Y	WO 89/05361 A1	(TALIM) see esp claim 1 & fig 1	1,11 at least
X	US 5487922	(HUGHES) see esp col5 lines 14-24 & 43-53, col6 lines 46-55 & ex 1	1,11 at least
X	US 5436035	(ALUSUISSE) see esp col4 line 59 - col5 line 17 & fig 1	1,11 at least
X	US 4941430	(NIHON) see esp col4 lines 8-28 & figs	1,11 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



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16.

Application No: GB 9706538.7  
Claims searched: 1-20

Examiner: Peter Beddoe  
Date of search: 23 April 1998

Category	Identity of document and relevant passage	Relevant to claims
Y	US 4269137 (XEROX) see esp coll line 54 - col2 line 8, col9 lines 23-46 & figs`	1,11 at least

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